Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **25 August 2017**

Candidates answer on separate paper. **2 hours**

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Suggested Solutions

Section A

Answer **all** the questions in this section.

1 *Use of the Data Booklet is relevant to this question.*

(a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$$

A student carried out the following experiment to determine the concentration of ethanol in a brand of wine.

A 10.0 cm^3 sample of the wine was diluted to 250 cm^3. He then added 25.0 cm^3 of 0.156 mol dm^{-3} $K_2Cr_2O_7$(aq) and excess dilute H_2SO_4 to a 25.0 cm^3 portion of the diluted solution. After allowing the mixture to stand for about an hour at room temperature, the excess $K_2Cr_2O_7$ in the mixture was then titrated with 0.118 mol dm^{-3} $(NH_4)_2Fe(SO_4)_2$(aq) using an appropriate indicator. At the end-point of the titration, he used 12.25 cm^3 of the Fe^{2+}(aq) solution.

(i) Write an ionic equation for the reaction that occurs during titration. [1]

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(ii) Calculate the concentration, in mol dm^{-3}, of ethanol in this brand of wine. [4]

mol of excess $Cr_2O_7^{2-}$ = $\frac{1}{6}$ × mol of Fe^{2+} used in titration

= $\frac{1}{6}$ × 0.118 × $\frac{12.25}{1000}$

= 2.41×10^{-4} mol

mol of $Cr_2O_7^{2-}$ added initially = cV = 0.156 × $\frac{25.0}{1000}$

= 3.90×10^{-3} mol

mol of $Cr_2O_7^{2-}$ that react with CH_3CH_2OH = $(3.90 \times 10^{-3}) - (2.41 \times 10^{-4})$

= 3.66×10^{-3} mol

$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$

mol of CH_3CH_2OH in 25.0 cm^3 of diluted soln = $\frac{3}{2}$ × mol of $Cr_2O_7^{2-}$ reacted

= $\frac{3}{2} \times 3.66 \times 10^{-3}$

= 5.49×10^{-3} mol

mol of CH_3CH_2OH in 250 cm^3 of diluted soln = $\frac{250}{25.0} \times 5.49 \times 10^{-3}$

= 0.0549 mol

Since 10.0 cm^3 of the sample of spirit was diluted to 250 cm^3,

$\therefore$ mol of CH_3CH_2OH in 10.0 cm^3 of spirit = 0.0549 mol

$\Rightarrow$ [CH_3CH_2OH] in the brand of spirit = $\frac{1000}{10.0}$ × 0.0549

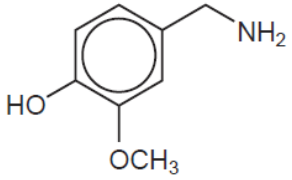
= 5.49 mol dm^{-3}

(b) The relatively high alcohol content in wine makes it difficult to pair wine with spicy food because the combination can create a painful burning sensation on the lips and tongue that cannot be wiped or rinsed away.

Capsaicin, $C_{18}H_{27}NO_3$, is the active ingredient in spicy food that gives the hot taste of chilli peppers. The structure of capsaicin can be deduced from the following reactions.

When capsaicin is boiled with dilute sulfuric acid, compound **A**, $C_{10}H_{18}O_2$, and the salt of compound **B**, are produced. Compound **B**, $C_8H_{11}NO_2$, has the structure shown, where the $CH_3O–$ group can be regarded as inert.

compound **B**



When **A** is heated with concentrated acidified $KMnO_4$, compound **C**, $C_6H_{10}O_4$, and compound **D**, $C_4H_8O_2$, are produced. **C** can be prepared from $Br(CH_2)_4Br$ in two steps whereas **D** can be prepared directly from $(CH_3)_2CHCH_2OH$.

Compounds **A**, **C** and **D** all react with aqueous sodium carbonate.

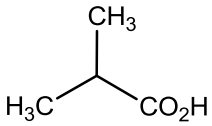
(i) What observations and deductions could be made from the reaction of **A**, **C** and **D** with aqueous sodium carbonate? [2]

effervescence of CO_2 ; A, C and D are acidic/contains $–CO_2H$ group.

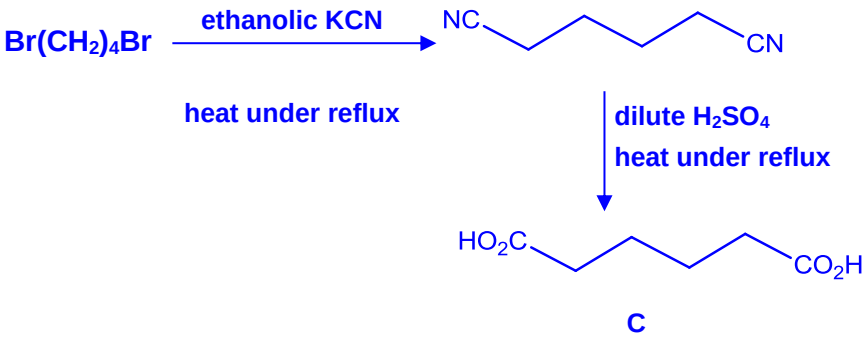
(ii) Draw the structural formula of **D** and state the reagents and conditions required for its preparation from $(CH_3)_2CHCH_2OH$. [2]

$K_2Cr_2O_7$ + dil. H_2SO_4; heat under reflux

D is



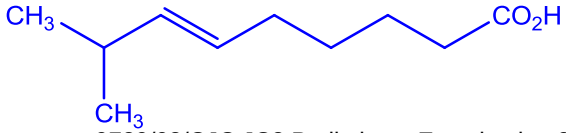
(iii) Show how compound **C** can be prepared from $Br(CH_2)_4Br$, stating clearly the reagents and conditions required for each step, and give the structural formulae of **C** and the intermediate formed. [4]



C

(iv) Hence suggest the structure for **A** and two possible structures for capsaicin. [3]

A is



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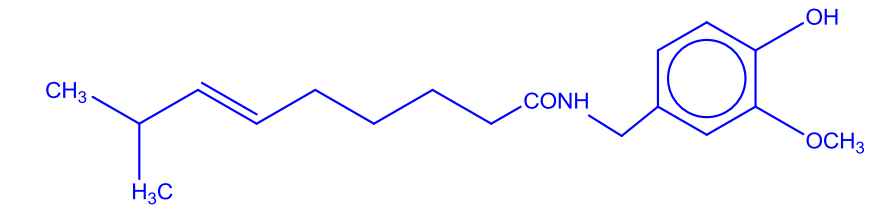
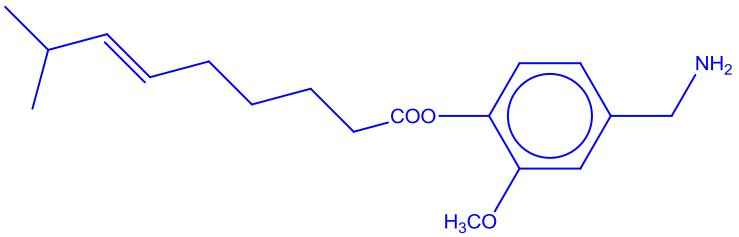
capsaicin is



and



(c) Methanol, CH_3OH, is the simplest alcohol that could be used to power a fuel cell in an electric car.

Figure 1.1 shows a preliminary design of a methanol fuel cell. The fuel and oxygen are fed continuously to the two electrodes which are made of platinum. Methanol is oxidised when the fuel cell is operated.

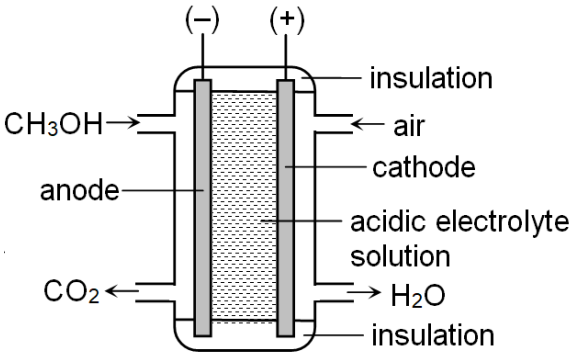


Fig. 1.1

(i) Write balanced equations for the half reactions at each electrode and for the overall cell reaction. [2]

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Anode: $CH_3OH(l) + H_2O \rightarrow CO_2(g) + 6H^+ + 6e^-$

Overall reaction: $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

(ii) Write a cell representation, indicating clearly on the cell representation the direction of electron flow in the external circuit. [1]

e^- flow

$Pt(s) \mid CH_3OH(l)/CO_2(g) \,//\, O_2(g)/ H_2O(l), H^+(aq) \mid Pt(s)$

(iii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline electrolyte. [1]

In an acidic medium, $E^{\ominus}_{O_2/H_2O}$ = +1.23 V

In an alkaline medium, $E^{\ominus}_{O_2/OH^-}$ = +0.40 V

Acidic electrolyte is preferred because oxygen is a <u>stronger oxidising agent</u> in an acidic medium.

(iv) The design of the above fuel cell could be improved by replacing the acidic electrolyte solution with a film of solid H^+ ion-conducting polymer.

Suggest a reason for doing so. [1]

Using a film of solid H^+ ion-conducting polymer as electrolyte would eliminate the possibility of acid leakage from the fuel cell.

(v) Methanol could also be used as fuel in an internal combustion engine.

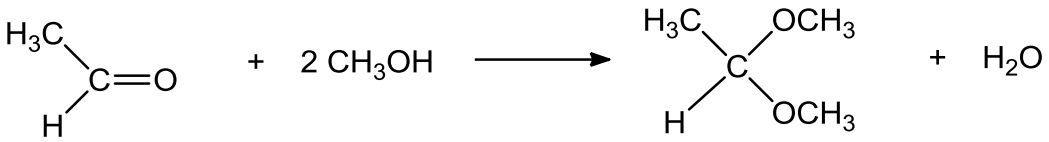
Suggest one advantage of the methanol fuel cell over such an internal combustion engine that uses methanol. [1]

In the methanol fuel cell, there is complete combustion of CH_3OH and so, no C nor CO (atmospheric pollutants) is produced.

[Total: 22]

[Turn over

2 Acetals are molecules that contain 2 –OR groups bonded to the same carbon and are formed when aldehydes are reacted with an alcohol in the presence of an acid. The reaction between ethanal and methanol in the presence of acid, to produce acetal **A** was studied.



acetal **A**

(a) When the initial rate of this reaction was measured at various starting concentrations of ethanal, methanol and H^+, the following results were obtained:

Experiment number	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.32	0.05	4.00
4	0.10	0.16	0.10	1.60

(i) Use the data in the table to determine the order with respect to

I ethanal

By inspection
Using experiments 1 and 2,
when $[CH_3CHO]$ increased by 0.25/0.20 = 1.25 times and the concentration of other reactants remain constant, the relative rate increases by 1.25 times.
Order of reaction wrt ethanal = 1

II methanol and

By inspection
Using experiments 2 and 3,
when $[CH_3OH]$ increased by 0.32/0.1 = 3.2 times and the concentration of other reactants remain constant, the relative rate increases by 4.00/1.25 = 3.2 times.
Order of reaction wrt ethanal = 1

III H^+.

[3]

By inspection
Using experiments 1 and 4,
when $[CH_3CHO]$ is halved and $[CH_3OH]$ is increased by 0.16/0.1 = 1.6 times, relative rate should be 0.8 since orders of reaction wrt ethanal and methanol are 1. However, the relative rate is 1.60 which means when the $[H^+]$ is doubled, rate is doubled.
Order of reaction wrt H^+ = 1

Alternatively, mathematical method
Let n be the order of reaction wrt H^+
$rate_{exp1} = k[ethanal]_{exp1}[methanol]_{exp1}[H^+]^n$

$1.00 = k(0.20)(0.10)(0.05)^n$---- (1)
$rate_{exp2} = k[ethanal]_{exp2}[methanol]_{exp2}[H^+]^n$
$1.60 = k(0.10)(0.16)(0.10)^n$---- (2)
(2) ÷ (1)
$1.6 = (0.5)(1.6)(2)^n$
n = 1

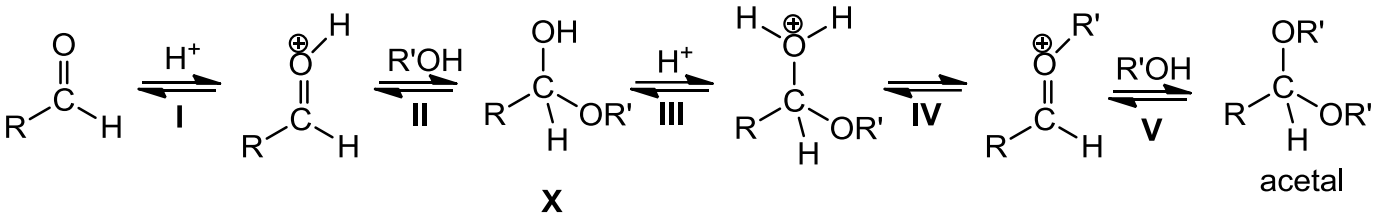
(ii) Use your results from **(a)(i)** to write the rate equation for the reaction. [1]

rate = $k[CH_3CHO][CH_3OH][H^+]$

(iii) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}. [1]

rate will be 2 × 4 = 8 times as fast as reaction 1 (i.e. relative rate = 8)

(b) The mechanism of acetal formation is proposed to proceed through the following steps.



(i) The protonation of the carbonyl group in step **I** is necessary for step **II** to take place. Suggest a reason for this. [1]

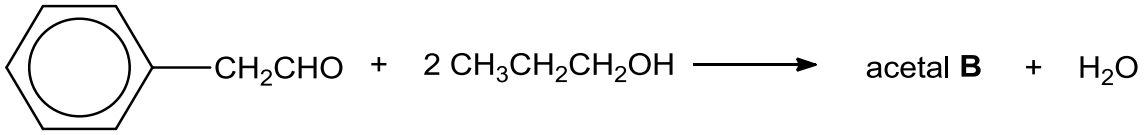
The protonation of the carbonyl group makes the carbonyl carbon more electron deficient (greater partial positive charge on carbonyl carbon) and thus more susceptible for the alcohol to attack.

(ii) Using your answer to **(a)(ii)**, state with reasons, which one is the rate-determining step of the reaction mechanism. [2]
Step II
Based on the rate equation, the slow step should involve 1 molecule of the carbonyl compound, 1 H^+ ion and 1 alcohol molecule

(iii) The species in the mechanism have various roles. They can be reactants, products, catalysts or intermediates. Suggest, with a reason in each case, the roles of H^+ and **X**. [2]
H^+ is a catalyst as H^+ is regenerated in steps II and V

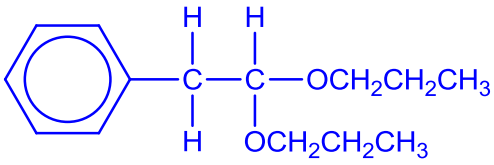
X is an intermediate as it is being produced in step II but used in step III .

(c) Draw the structure of the acetal **B** formed from the reaction between phenylethananl and propan-1-ol.



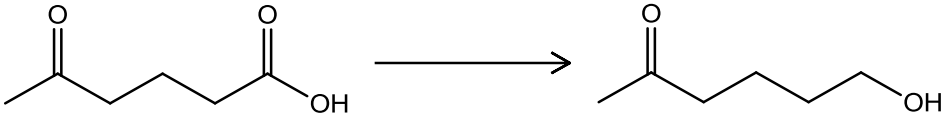
[1]

[Turn over

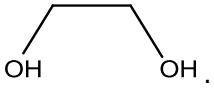


(d) Acetal formation is useful in organic synthesis. When an aldehyde or ketone is converted to an acetal, the carbonyl group is protected from attack by reagents such as bases and reducing agents. The acetal can later be hydrolysed by a strong acid to form the original aldehyde or ketone since the formation of acetals is a reversible reaction.

Suggest a suitable synthesis route for the following conversion



which involves the initial formation of an acetal group using ethane-1,2-diol,



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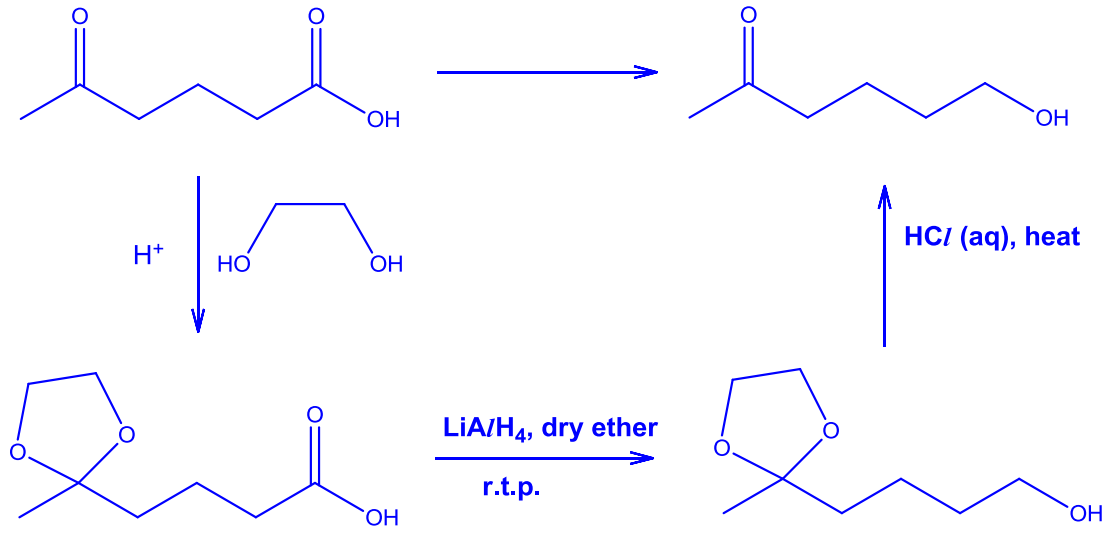
[2]



(e) Methanol is currently studied as a potential green fuel that greatly reduces the pollution to the environment.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

(i) The standard molar entropy, $S^{\ominus}$ is the entropy content of one mole of substance under standard conditions. Given the following standard molar entropy values, calculate the standard entropy change of combustion of methanol. [1]

	$S^{\ominus}$ /J K^{-1} mol^{-1}
$CH_3OH(l)$	126.8

$O_2(g)$	205.0
$CO_2(g)$	213.6
$H_2O(l)$	69.9

$\Delta S_c^{\ominus}$ $CH_3OH(l)$ = $S^{\ominus}_{products} - S^{\ominus}_{reactants}$

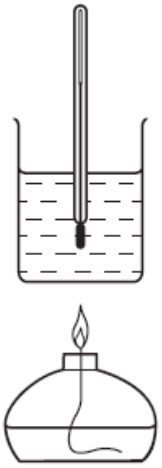
= 213.6 + 2 x 69.9 – (126.8 + 3/2 x 205)

= – 80.9 J K^{-1} mol^{-1}

(ii) Hence, explain the significance of the sign of the standard entropy change of combustion of methanol. [1]

The standard entropy change of combustion reaction has a negative sign. Since the amount of gaseous particles produced is less than the initial amount, there is a decrease in the number of ways to arrange the gaseous particles, giving rise to a decrease in disorder.

(iii) A student carried out an experiment to determine the enthalpy change for the combustion of methanol. A sample of methanol was burnt under laboratory conditions and the following results were obtained by the student.



initial temperature of the water	25.0 °C
final temperature of the water	48.2°C
mass of alcohol burner before burning	259.65 g
mass of alcohol burner after burning	259.15 g
mass of glass beaker and water	150.00 g
mass of glass beaker	50.00 g

Given that the theoretical enthalpy change of combustion of methanol is -726 kJ mol^{-1}, calculate the percentage of heat evolved used to heat up the water. [2]

(Experimental) Heat absorbed by water = (150 – 50)(4.18)(48.2 – 25)

[Turn over

= 9697.6J

Theoretical heat evolved by combustion of methanol = 726 000 x $\frac{0.5}{32}$ = 11343J

% of heat evolved used to heat up the water = 9697.6 / 11343 x 100 = 85.5%

(iv) Using the theoretical enthalpy change of combustion and other relevant information given above, calculate the change in standard Gibbs free energy for the combustion reaction. [1]

$\Delta G_c^o = \Delta H_c^o - T\Delta S_c^o$
$= -726 - (298)(-80.9/1000)$
$= -702\ kJmol^{-1}$

(v) Predict and explain the effect on the spontaneity of this reaction of increasing the temperature. [2]

$\Delta G = \Delta H - T\Delta S$
ΔH is negative while $-T\Delta S$ is positive. Increasing the temperature increases the magnitude of $-T\Delta S$ and ΔG becomes more positive.
Thus, reaction becomes less spontaneous .

[Total: 20]

3 **(a)** Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that consumes it. In 2008, a cholera outbreak in Zimbabwe occurred due to a lack of proper water treatment. It is possible to stop the spread of cholera by treating water with chlorine or solid calcium chlorate(I). Calcium chlorate(I), $Ca(ClO)_2$, reacts with water to form chloric(I) acid, $HClO$, which acts as a general biocide.

(i) Write an ionic equation for the reaction of calcium chlorate(I) with water. [1]

$ClO^- + H_2O \rightleftharpoons HClO + OH^-$

(ii) Chloric(I) acid, $HClO$, can also be formed by adding chlorine dioxide gas, ClO_2, to water as shown in the equation below:

$$4ClO_2 + 2H_2O \rightarrow HClO + HClO_3$$

Identify the specific type of reaction that chlorine has undergone by stating the oxidation states of chlorine in the relevant species. [2]

Disproportionation reaction

$4ClO_2 + 2H_2O \rightarrow HClO + HClO_3$

+4 +1 +5

(iii) An environmental scientist decides to analyse a sample of treated water to find out the amount of chlorine it contains. A 250 cm^3 sample of the chlorine containing water was treated with an excess of potassium iodide solution.

$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$

The sample was subsequently titrated with 12.30 cm^3 of 0.001 mol dm^{-3} sodium thiosulfate solution to find out how much iodine had been formed.

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

Calculate the concentration of Cl_2, in mol dm^{-3}, in the original sample of treated water. [2]

No. of moles of $S_2O_3^{2-}$ = $\frac{12.30}{1000} \times 0.001$

= 1.23×10^{-5} mol

Since $I_2 \equiv 2S_2O_3^{2-}$,

No. of moles of I_2 formed = $\frac{1}{2} \times 1.23 \times 10^{-5}$

= 6.15×10^{-6} mol

[Turn over

Since $ClI_2 \equiv I_2$,

Concentration of $ClI_2 = \frac{1000}{250} \times 6.15 \times 10^{-6}$

$= 2.46 \times 10^{-5}$ mol dm^{-3}

(iv) Suggest a reason why it may be preferable to use calcium chlorate(I) rather than chlorine for treating drinking water. [1]

calcium chlorate(I) is a solid which makes it easier and safer to handle compared to chlorine gas.

or calcium chlorate(I) is more soluble in water than chlorine.

(b) The extraction of aluminium from its ore is highly energy intensive and often results in pollution of the environment. Phosphorus, however, poses a threat to biodiversity in aquatic ecosystems through the depletion of oxygen via the excessive growth and decomposition of aquatic plants and algae.

When heated in chlorine, both aluminium and phosphorus form chlorides.

(i) Describe the observations when a **limited** amount of water is added to the chlorides of aluminium and phosphorus respectively and write equations for any reactions that occur. [2]

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$
[white ppt & white fumes observed]

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$
[white fumes observed]

(ii) Write equations for any reactions that might occur when an **excess** amount of water is added to the chlorides of aluminium and phosphorus respectively and suggest the pH of each solution formed. [2]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

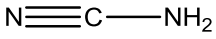
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$

pH 3

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

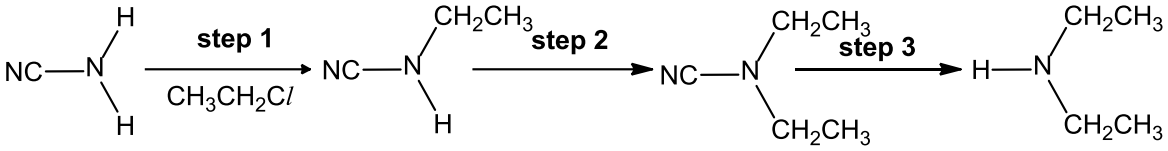
pH 1-2

(c) Cyanamide, CH_2N_2, is a compound commonly used in fertilisers that could also cause eutrophication, which deplete the water's oxygen supply through excessive growth and decomposition of algae and water plants.



cyanamide

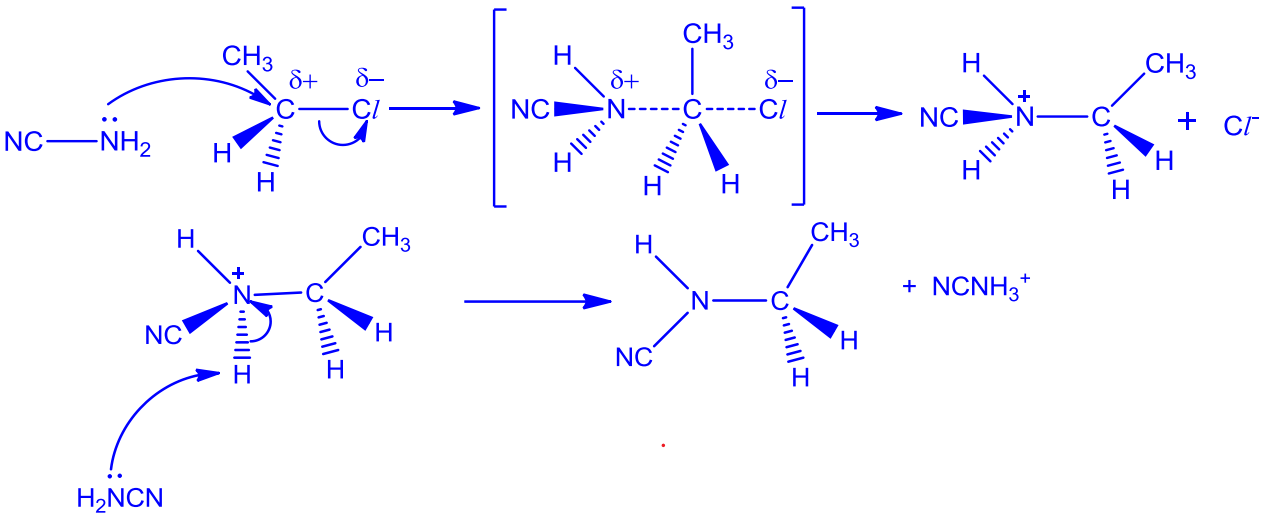
Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.



N-ethylethylamine

(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

Mechanism: Nucleophilic substitution reaction (S_N2)



(ii) Identify the two roles of cynnamide in your mechanism. [1]

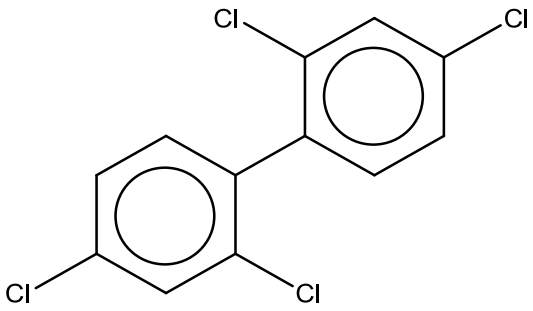
Nucleophile and Base

(iii) Besides using a specific catalyst and heating under reflux for steps 1 and 2, suggest another condition which would allow a high yield of the intermediate formed in step 2. [1]

Excess CH_3CH_2Cl

(d) 2,2',4,4'-tetrachlorobiphenyl is a common organic pollutant that is immiscible in water.

[Turn over



2,2',4,4'-tetrachlorobiphenyl

Suggest two reasons why 2,2',4,4'-tetrachlorobiphenyl is typically inert and chemically unreactive to nucleophilic reagents. [2]

The p-orbital of the chlorine atoms overlap with the π electron cloud system of the benzene rings. The lone pair of electrons on each C*l* atom is delocalised into the benzene rings. This results in the C–C*l* bond having a partial double-bond character which makes the C–C*l* bond stronger and less ready to undergo reaction.

The C of the C–C*l* bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

[Total: 18]

Section B

Answer **one** question from this section.

4 Transition elements show unique properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) Chromium, a transition element, forms two common series of compounds. One containing chromium in the +3 oxidation state while the other containing chromium in +6 oxidation state.

The complex ion $[Cr(OH)_6]^{3-}$ is green whereas the complex ion $[Cr(NH_3)_6]^{3+}$ is purple. Both of these complexes are octahedral.

In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(i) Using the Cartesian axes, like those shown in Fig 4.1, draw fully-labelled diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex. Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram upper.

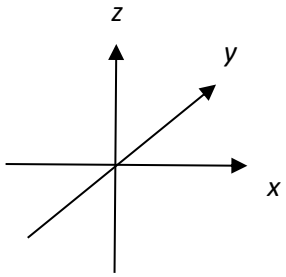
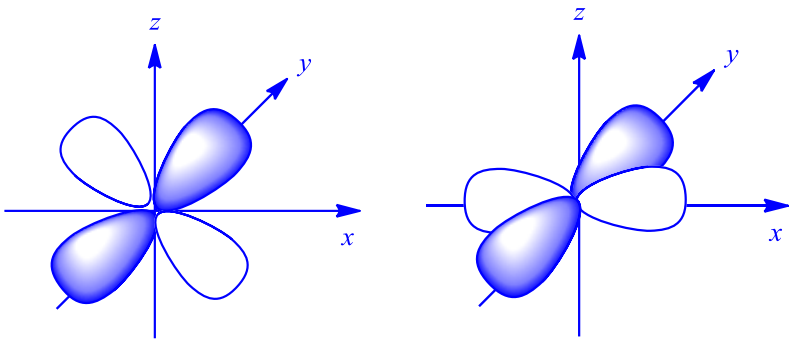


Fig. 4.1

[2]



lower d-orbital upper d-orbital

[Turn over

(ii) Explain why splitting of the d-subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)(i).** [2]

During formation of an octahedral complex, the ligands would approach the central metal ion with partially filled d-subshell along the x, y and z axes.

As the ligands would approach the $d_{x^2-y^2}$ and d_{z^2} orbitals 'head-on' (along the x, y and z axes), the inter-electronic repulsion is stronger between the ligands and the d_{z^2} and $d_{x^2-y^2}$ orbitals.

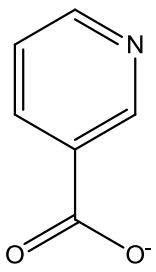
The ligands approach the d_{xy}, d_{xz} and d_{yz} orbitals between the orbital lobes (between the x, y and z axes). Hence the inter-electronic repulsion is not as strong between the ligands and the d_{xy}, d_{xz} and d_{yz} orbitals.

Hence the splitting of the degenerate d orbitals into two slightly different energy levels with a small energy gap will occur.

(iii) By considering your answer to **(a)(ii)**, suggest why $[Cr(OH)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ have different colours. [1]

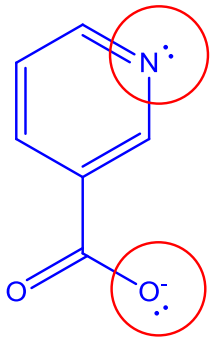
$[Cr(OH)_6]^{3-}$ complex has a different d-d* energy gap from $[Cr(NH_3)_6]^{3+}$ complex, hence visible light of different wavelength / frequency is absorbed during d-d* transition in both complexes.

(b) Chromium(III) nicotinate is commonly used as chromium supplementation for medical conditions associated with diabetes mellitus type 2. This octahedral complex contains three nicotinate ions per chromium ion. The nicotinate ion has the structure shown below.



nicotinate ion

(i) Copy the structure of nicotinate ion and circle the atoms that are bonded to chromium(III) ion. Explain your choice of atoms. [2]



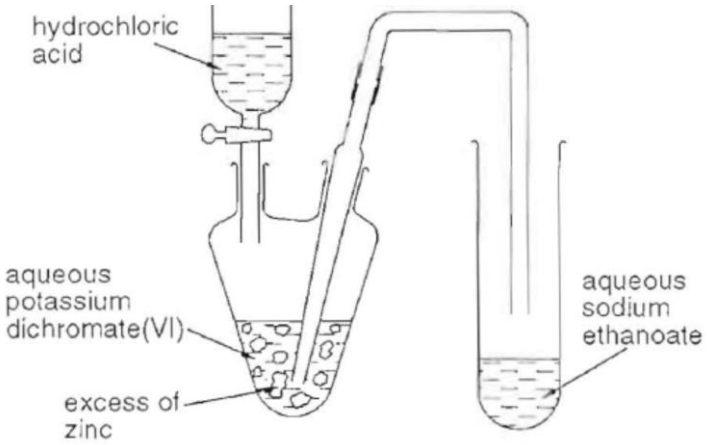
Presence of lone pairs of electrons on both N and O^- which allows nicotinate ion to donate two lone pairs of electrons to form a stable 6-membered ring structure with the central Cr^{3+} ion.

(ii) What is the overall charge of this complex? [1]

0 / no charge

(c) Chromium-containing compounds are useful reagents in the laboratory.

The apparatus and reagents shown in the diagram are used to prepare chromium(II) ethanoate, which is a reducing agent.



All the acid is added to the dichromate solution and the zinc in the flask. The tap funnel is left open. The flask is shaken and chromium soon reaches the Cr^{3+} state.

(i) Write balanced equations for the **two** reactions involving zinc which take place initially in the flask. [2]

[Turn over

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$(Zn \rightarrow Zn^{2+} + 2e^-) \times 3$

$Cr_2O_7^{2-} + 3Zn + 14H^+ \rightarrow 2Cr^{3+} + 3Zn^{2+} + 7H_2O$

The colour of the solution in the flask subsequently changes as $Cr^{2+}(aq)$ is produced.

(ii) Using relevant redox potential values in the *Data Booklet*, show why the reduction of Cr^{3+} to Cr^{2+} is likely to proceed. [2]

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41$ V **(less negative)**

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V

Since $E^\ominus_{Cr3+/Cr2+}$ is less negative than $E^\ominus_{Zn2+/Zn}$,

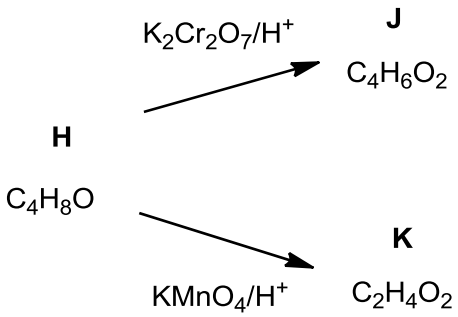
$E^\ominus_{cell} = -0.41 - (-0.76) = +0.35$ V **> 0 (spontaneous reaction)**

The tap funnel is subsequently closed and the liquid in the flask forced over into the tube containing the aqueous sodium ethanoate to form chromium(II) ethanoate.

(iii) By considering your answers to **(c)(i)**, suggest what causes the liquid to be forced over into the tube. [1]

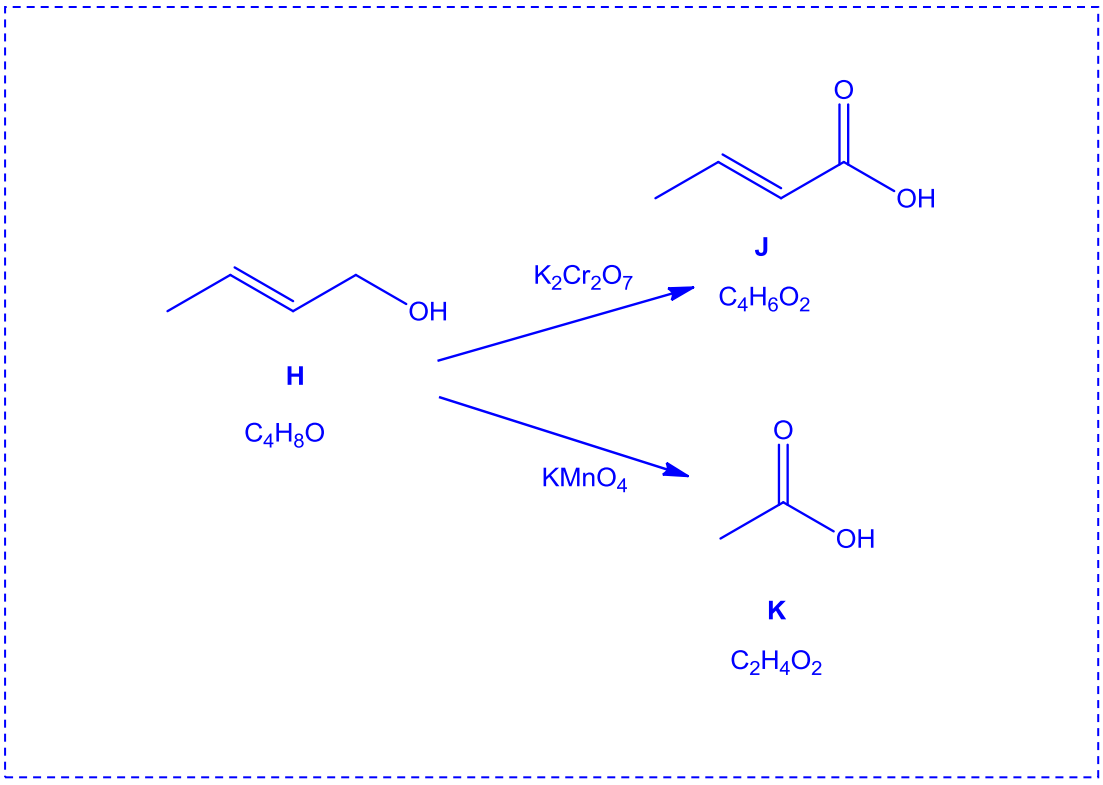
Build-up of pressure from the formation of $H_2(g)$ caused liquid to be forced over.

(d) Another chromium-containing compound, $K_2Cr_2O_7$, together with $KMnO_4$ are common oxidising agents used in organic synthesis. $KMnO_4$ is the more powerful of the two, as shown by the following scheme.

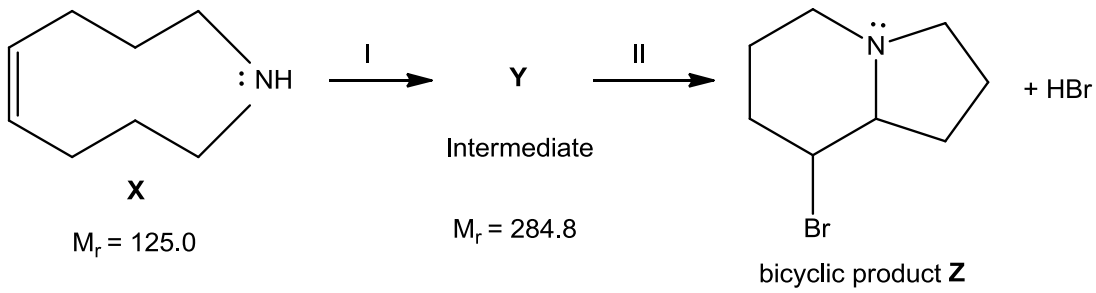


All three compounds, **H**, **J** and **K** react with sodium metal. **J** and **K** react with Na_2CO_3, but **H** does not. **H** and **J** decolourise aqueous bromine.

Suggest structures for **H**, **J** and **K**. [3]

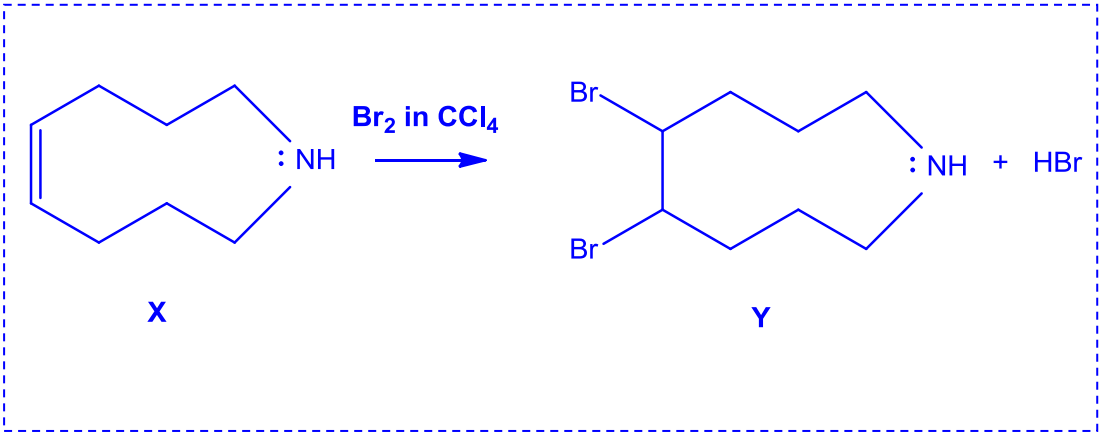


(e) The bicyclic product **Z** shown below can be formed from **X** in the following scheme:

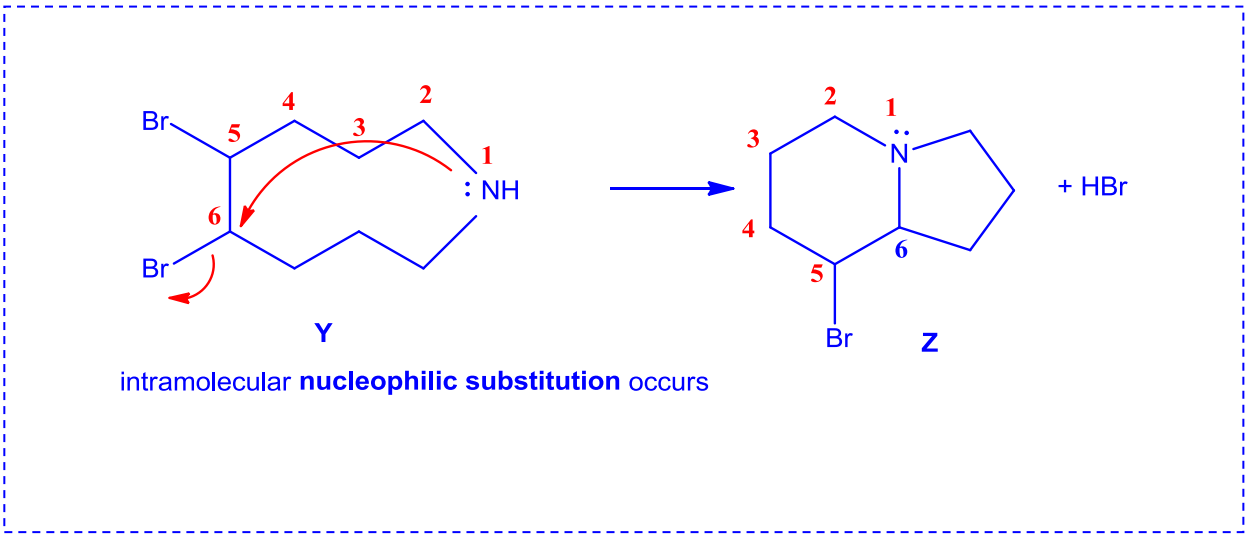


[Turn over

(i) Suggest reagents and conditions for Step I and the structure of **Y**. [2]



(ii) Given that Step II is an intramolecular reaction, explain the conversion of **Y** into **Z**, drawing curly arrows to show the movement of electron pair where necessary. State the type of reaction in Step II. [2]



[Total: 20]

5 Hydroformylation is used commercially for producing aldehydes from alkenes. The aldehyde produced is then converted into other organic compounds.

Butanal is synthesised from propene from the following hydroformylation reaction at 500 K.

$$CH_3CH{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CH_2CHO(g) \qquad \Delta H < 0$$

(a) An equimolar mixture of $CH_3CH{=}CH_2$, CO and H_2 at an initial total pressure of 150 atm is allowed to reach dynamic equilibrium. Figure 5.1 below shows the graphs of partial pressure of $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ against time.

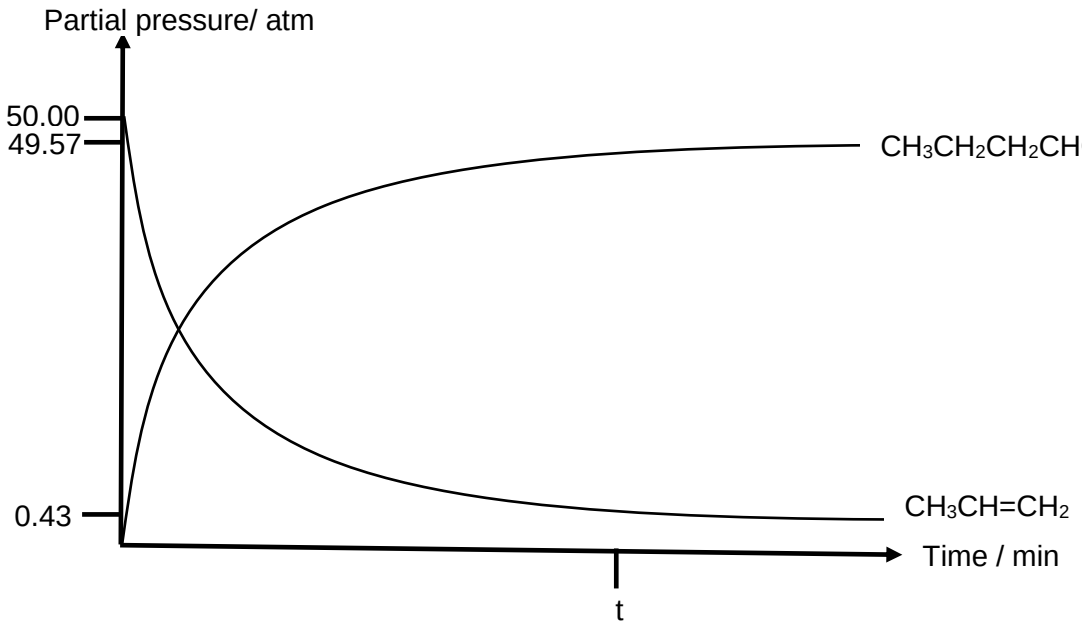


Figure 5.1

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the rates of forward and reverse reactions have become equal and there is no change in the concentration of the reactants and the products.

(ii) Write an expression for K_p for the above reaction. [1]

$$K_p = \frac{P_{CH3CH2CH2CHO}}{(P_{CH3CH=CH2})(P_{CO})(P_{H2})}$$

[Turn over

(iii) Using Figure 5.1 above, calculate K_p for the hydroformylation reaction at 500 K, stating its units. [3]

	$CH_3CH=CH_2(g)$ +	$CO(g)$ +	$H_2(g)$	⇌	$CH_3CH_2CH_2CHO(g)$
Initial Partial Pressure/ atm	**50**	**50**	**50**		**0**
Change in partial pressure/ atm	**- 49.57**	**- 49.57**	**- 49.57**		**+ 49.57**
Equilibrium Partial Pressure/ atm	**0.43**	**0.43**	**0.43**		**49.57**

$$\mathbf{K_p = \frac{49.57}{(0.43)(0.43)(0.43)} = 623.46\ atm^{-2}}$$

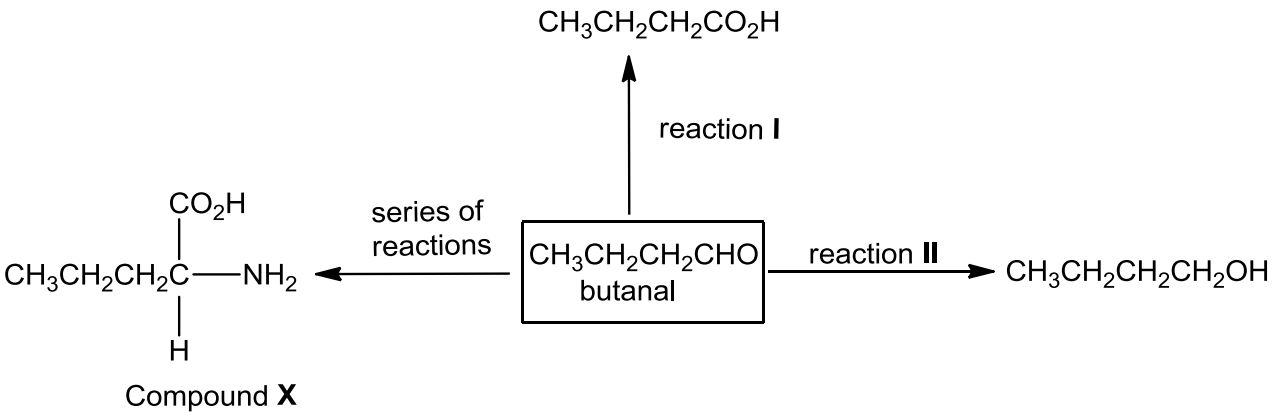
$$\mathbf{= 623\ atm^{-2}}$$

(iv) State how the graphs of partial pressure against time for $CH_3CH=CH_2$ and $CH_3CH_2CH_2CHO$ would differ from that shown in Figure 5.1 when the experiment is repeated at a higher temperature. [2]

The gradients of the graphs will be steeper Or the equilibrium will be established at a shorter time (before time t).

The equilibrium partial pressure of $CH_3CH_2CH_2CHO$ would decrease while the equilibrium partial pressure of $CH_3CH=CH_2$ will increase.

Butanal, synthesised from hydroformylation reaction, can undergo further reactions as shown in the reaction scheme below.

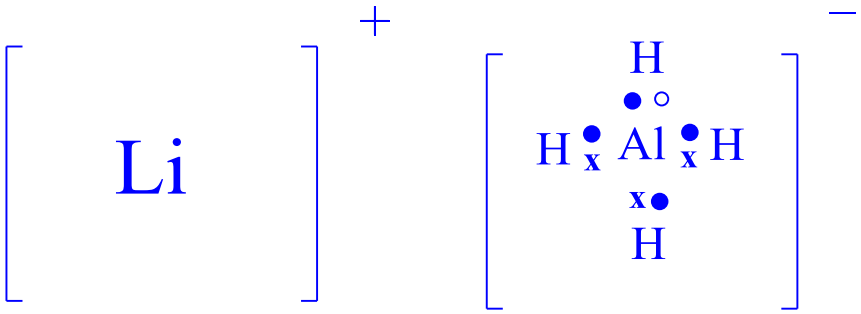


(b) From reaction **I** above, butanoic acid is produced. Comment on the difference in the solubility of butanal and butanoic acid in water. [2]

Butanoic acid is more soluble than butanal. Butanoic acid molecules contains both electron deficient H atoms as well as highly electronegative O atoms with lone pair of electrons, therefore they are able to form more extensive hydrogen bonds with water molecules on average as compared to butanal molecules which only contains highly electronegative O atoms with lone pair of electrons.

(c) In reaction **II**, butanal is reduced to give butan-1-ol. One of the commonly used reducing agents is lithium aluminium hydride, $LiAlH_4$, which is usually dissolved in dry ether.

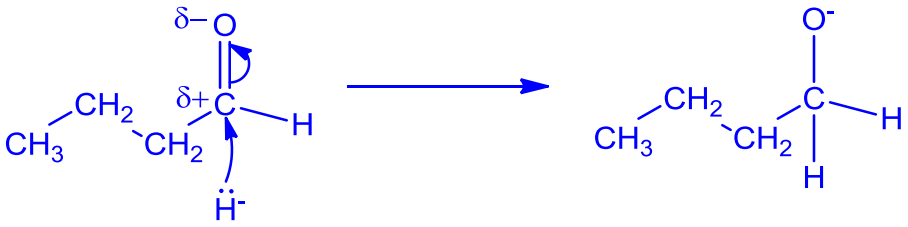
(i) Given that $LiAlH_4$ exist as $Li^+[AlH_4]^-$, draw the dot-and-cross diagram for $LiAlH_4$. [1]



(ii) The reaction between $LiAlH_4$ and butanal to form butan-1-ol happens in two-steps.

The first step involves a nucleophilic addition reaction between the hydride ion, H^-, from $LiAlH_4$ and butanal to form an anion.
The second step involves the protonation of the anion to form butan-1-ol.

Using the information above, show how the anion in the first step is formed with the use of curly arrows showing the movement of electrons and charges. [2]



(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used to convert butanal to butan-1-ol. By considering the chemical bonds in $LiAlH_4$ and $NaBH_4$, suggest why $LiAlH_4$ is a more powerful reducing agent $NaBH_4$. [1]

The size of Al atom is larger compared to B and the orbital overlap of Al and H is less effective. Thus the bond length of Al–H bond is longer than that of B–H bond and less energy is required to break the weaker Al–H bond, resulting in a greater ease of generating the H^- nucleophile. Or There is greater electronegativity difference between Al and H than B and H, therefore the tendency of forming H^- is higher in $LiAlH_4$ than $NaBH_4$.

[Turn over

(iv) State a reason why $LiAlH_4$ cannot be used to reduce alkenes even though it is a powerful reducing agent. [1]

The electron rich C=C will not attract the H^- nucleophiles.

(v) Expain how the rate of the reaction in **(c)(ii)** would differ if butanone is used in place of butanal. [2]

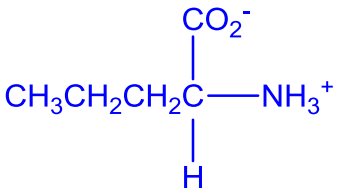
The rate of reaction will be slower with butanone.

In butanone, there are two electron-donating alkyl groups directly attached to the carbonyl carbon. Hence the partial positive charge on the carbonyl carbon in butanone is less pronounced than that in butanal which only has 1 alkyl group.

Or

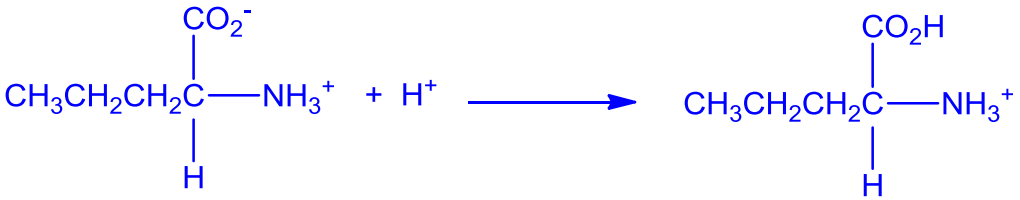
The presence of 2 alkyl groups in butanone contributes to greater steric hindrance.

(d) Draw the structure of the predominant form produced when compound **X** is in an aqueous solution of pH 7. [1]

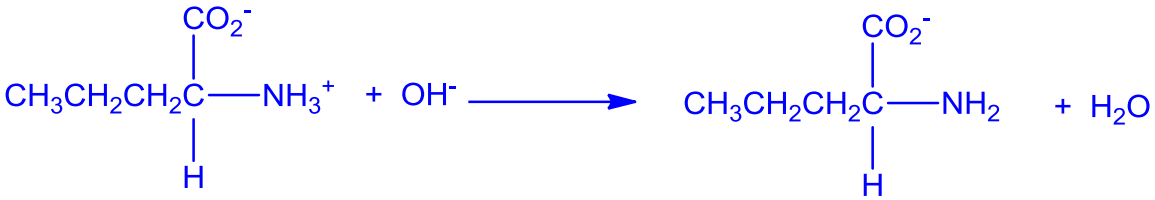


(e) Write two equations to show how the solution in **(d)** is able to resist the change in pH upon addition of small amounts of acid and base. [2]

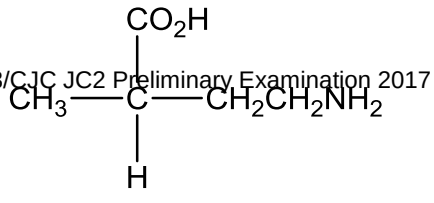
When small amounts of acid is added,



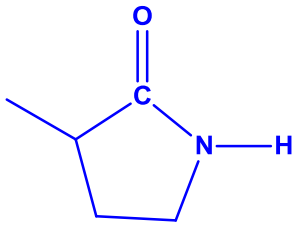
When small amounts of base is added,



(f) Compound **Y** is an isomer of compound **X**. Draw the structural formula of the **final** product when compound **Y** reacts with PCl_5. [1]



Final product formed:



[Total: 20]

[Turn over